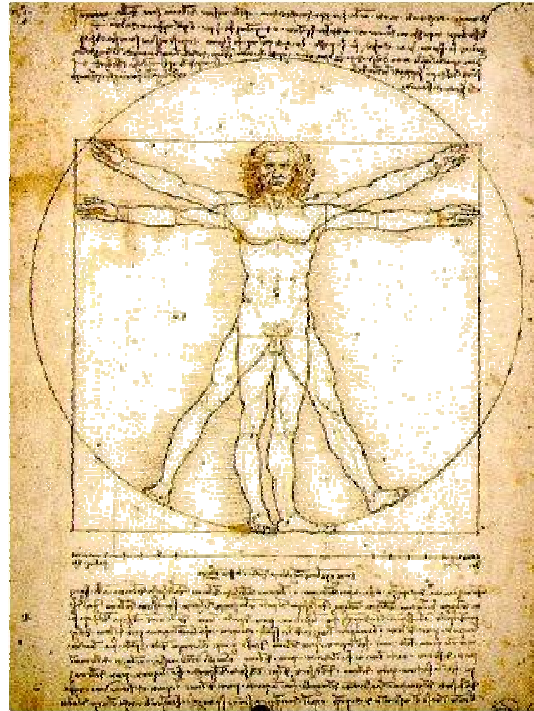


# Complex Functional Nanomaterials

Mission: *Integrate multiple materials and structures across nano- to macro- length scales to promote complex and collective interactions and develop new emergent behaviors and functions*

## Los Alamos

Arthur Ramirez  
Victor Klimov  
John Sarrao



## Sandia

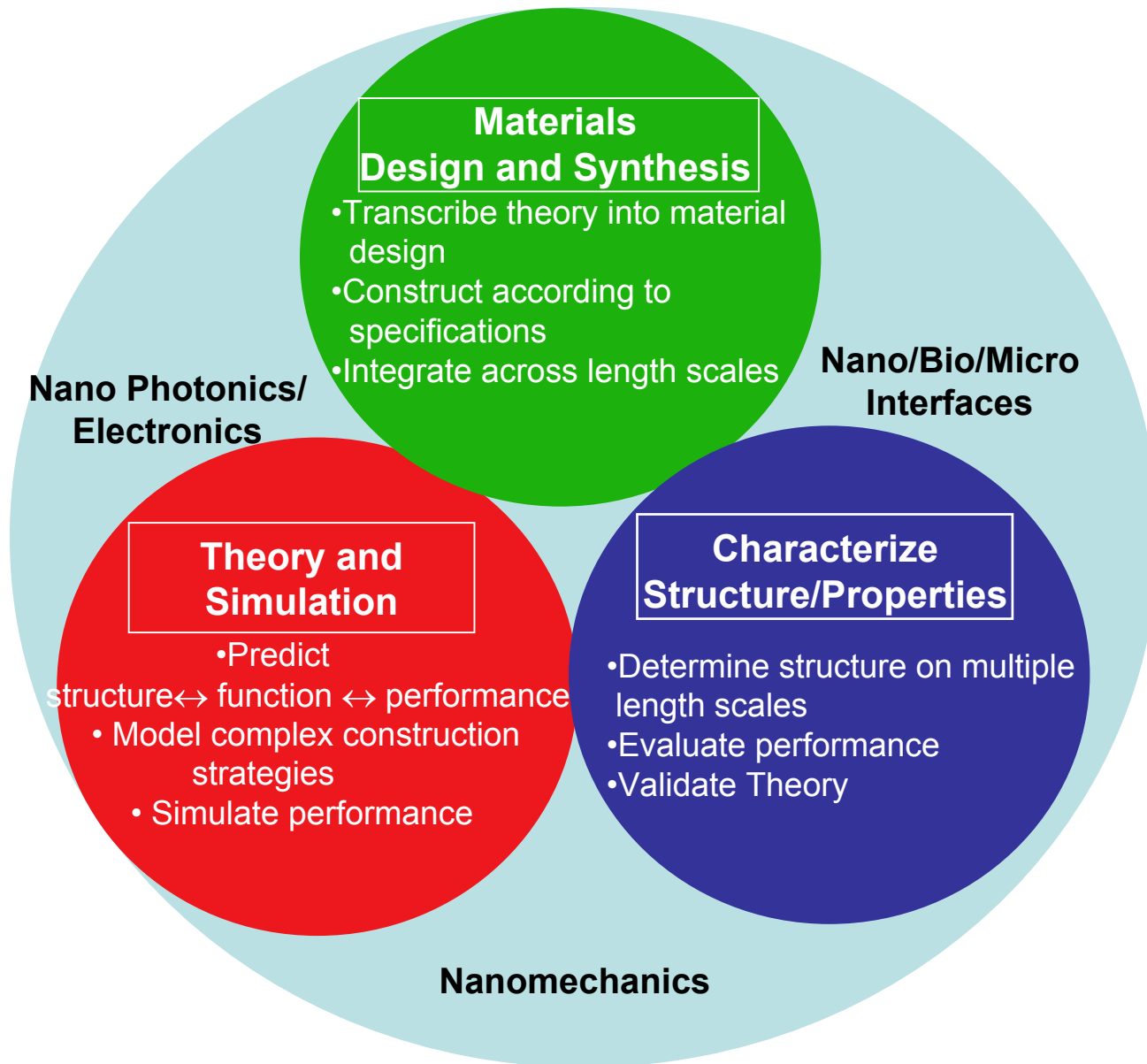
Jeff Brinker  
Frank van Swol  
Tim Boyle  
Paul Clem  
Jim Martin

*Living systems are  
multicomponent,  
hierarchical, and prioritized*

Can we develop useful complex functions normally associated with living systems into robust materials that we can integrate at the micro & macro scales?

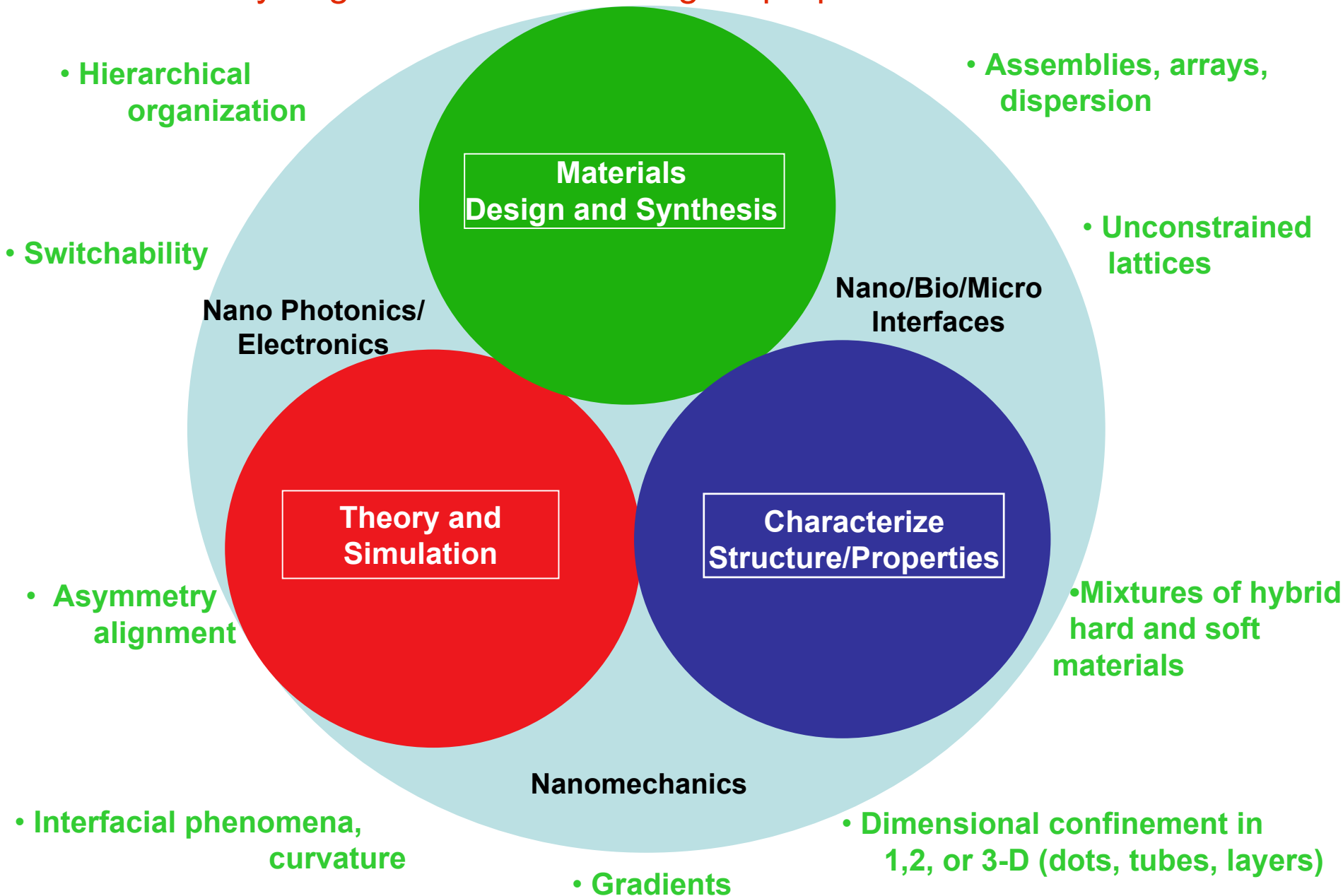
# Complex Functional Materials

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# Complex Functional Materials

Synergistic and often emergent properties arise due to:

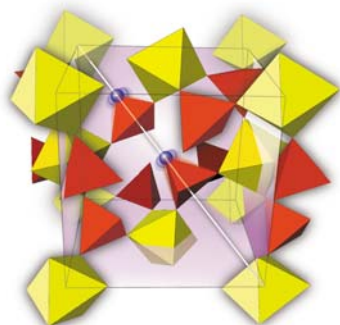


# CFN Thrust Will Explore Nano-Structured Materials Designed and Synthesized on Different Length Scales

## Nanocells

Many materials with unique functionality have complex, nm-scale crystal structures

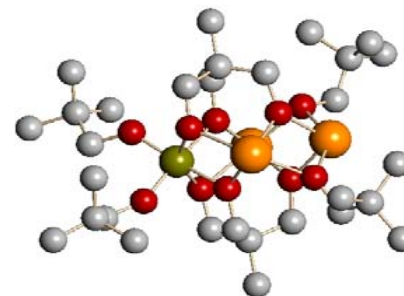
Novel precursor chemistries enable complex materials synthesis



Nanometer Unit Cell-  
 $\text{ZrW}_2\text{O}_8$

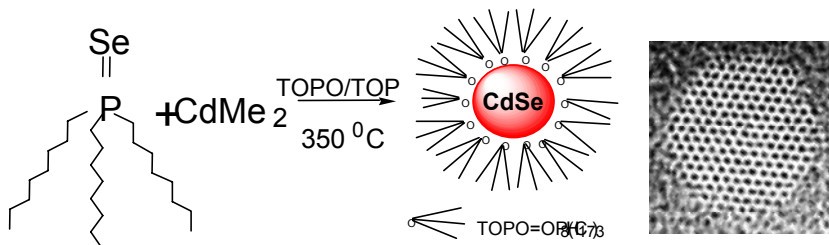
Underconstrained lattice

Negative Thermal  
Expansion

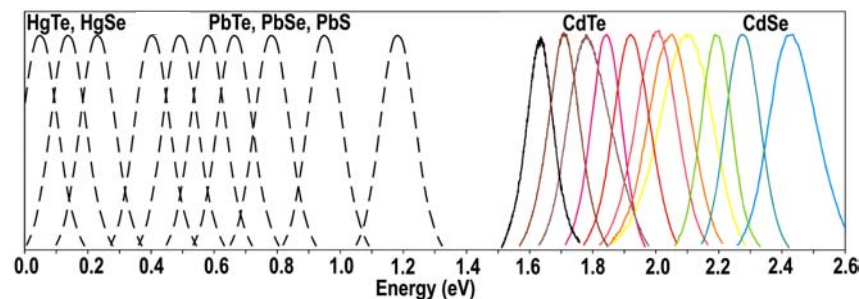


$(\text{m-THME})\text{Sn}_3\text{Ti}(\text{m-ONep})_2(\text{ONep})_2$

- Size, shape and composition control for tuning electronic and optical properties of quantum dot building blocks:

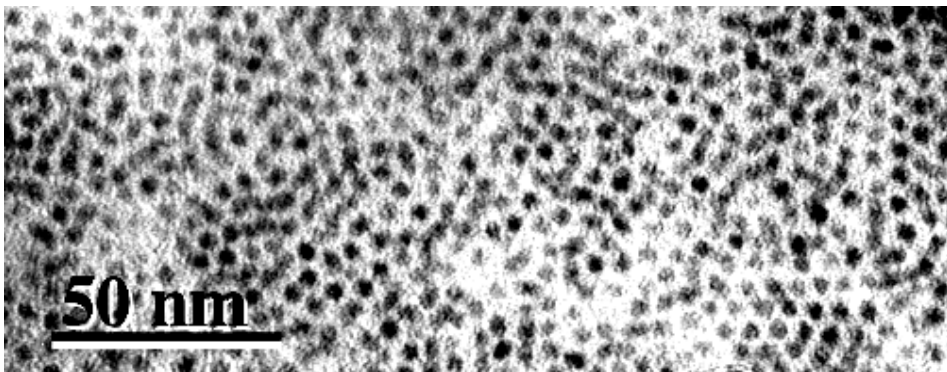


$R = 10\text{--}70 \text{ \AA}$ ,  $\delta R/R = 4\text{--}7\%$



Tunable emission via size and composition control

# Quantum Dot Molecules and Solids Represent New Types of Artificial Solids



$R = 12 \text{ \AA}$

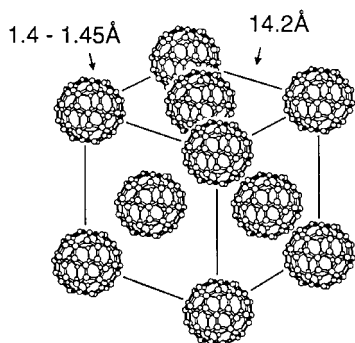
$15 \text{ \AA}$

$21 \text{ \AA}$

Solids of CdSe NQRs exhibit size dependent properties

Covalent linkages allow tailoring of electronic properties and directed energy transfer

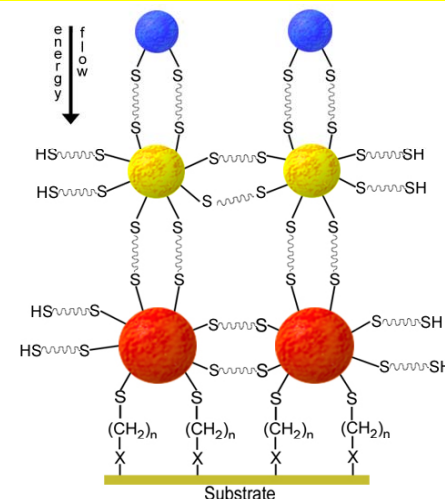
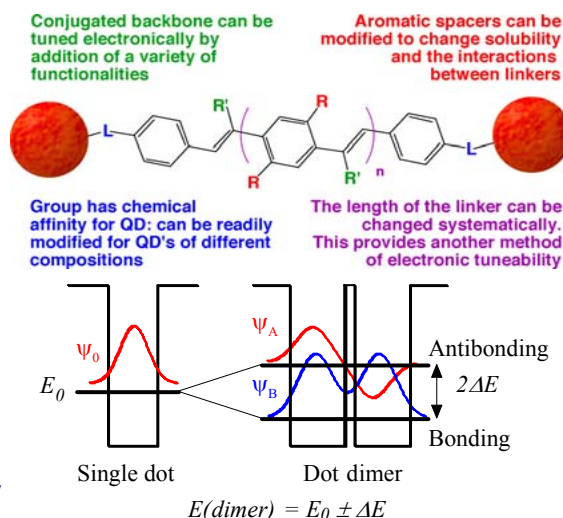
New electronic materials are enabling new functionality



Nanometer Unit  
Cell

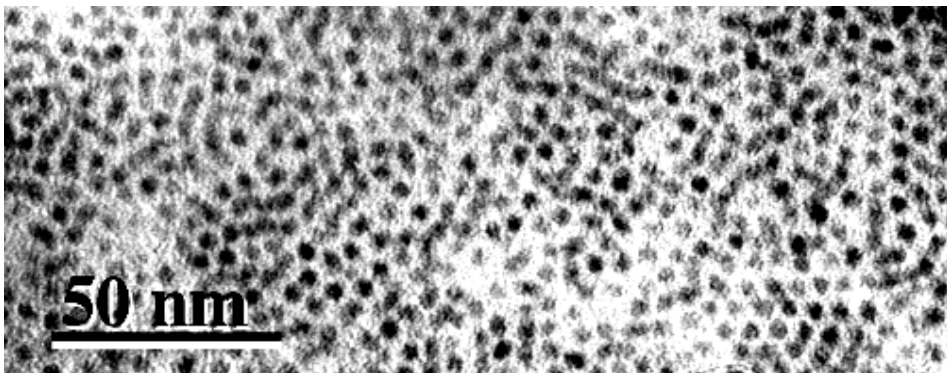
$C_{60}$  Curvature

Superconductivity



Gradient structure for directing energy flows

# Quantum Dot Molecules and Solids Represent New Types of Artificial Solids



$R = 12 \text{ \AA}$

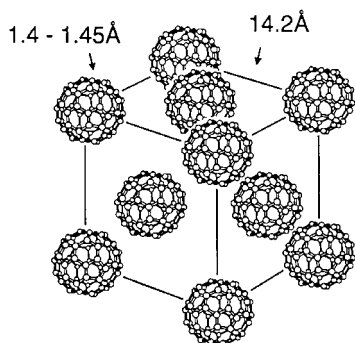
$15 \text{ \AA}$

$21 \text{ \AA}$

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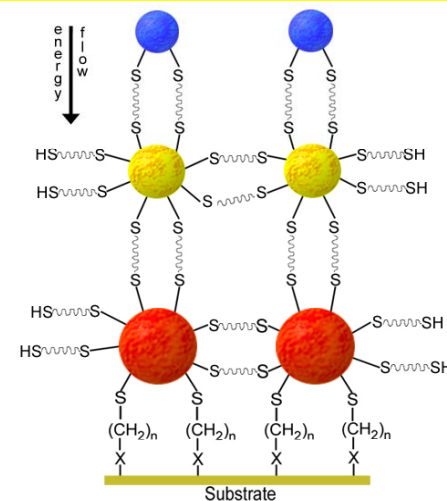
Nanometer Unit Cell

$C_{60}$  Curvature

Superconductivity

Rabi flopping in stacked conical InAs QD dimers

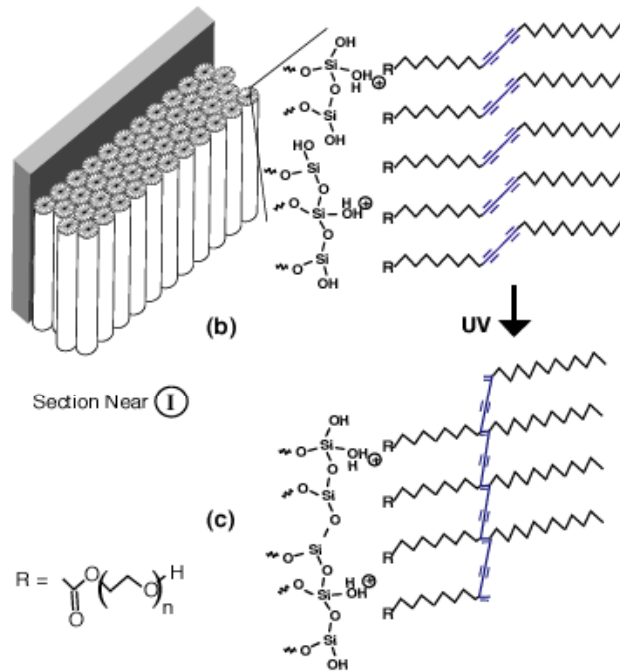
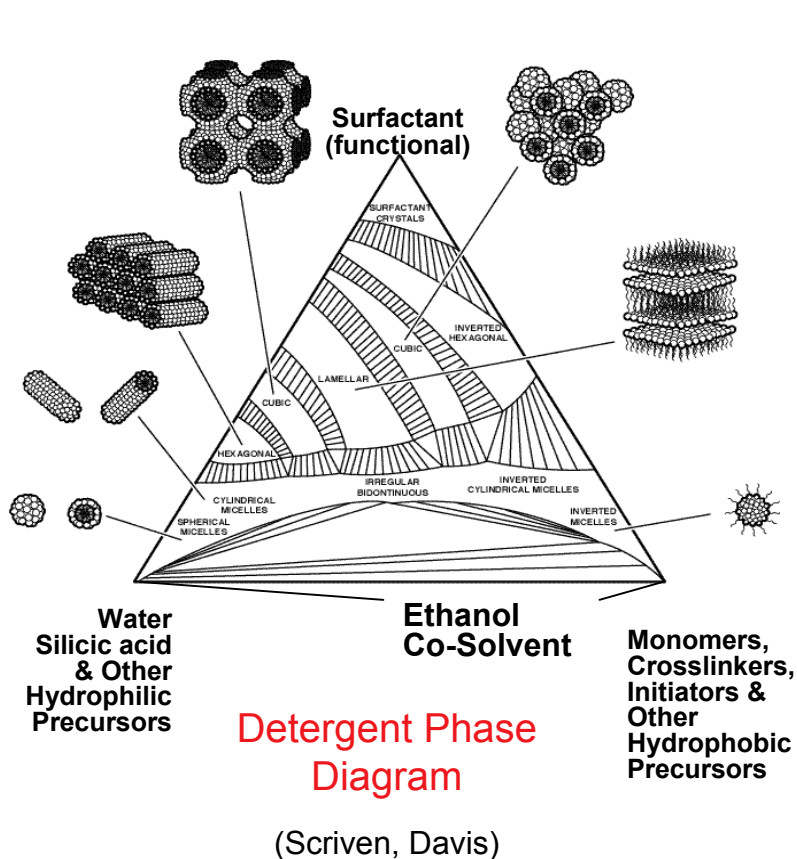
QuickTime™ and a Video decompressor are needed to see this picture.



Gradient structure for directing energy flows

# Materials Self-Assembly Across Multiple Length Scales

## Use polymerizable surfactants as structure-directing agents and monomers to create conjugated polymer nanocomposites



Self-assembly & topotactic polymerization  
Nanostructure aligns, protects, and mediates performance



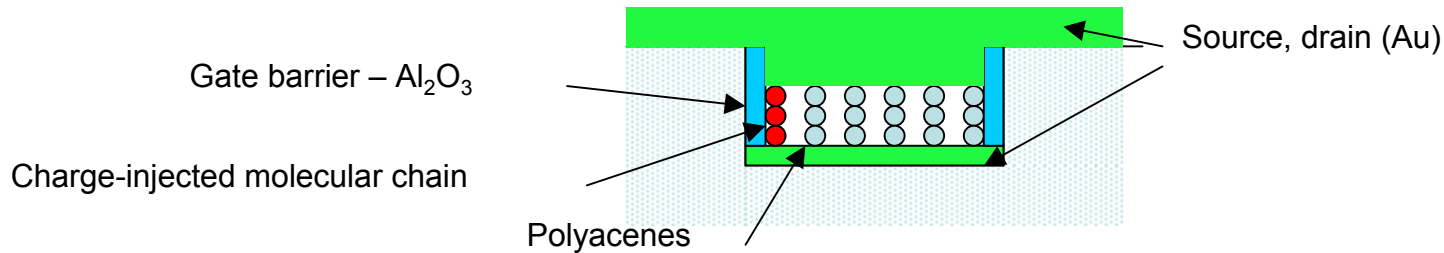
Heat  
Stress  
Chemical Exposure



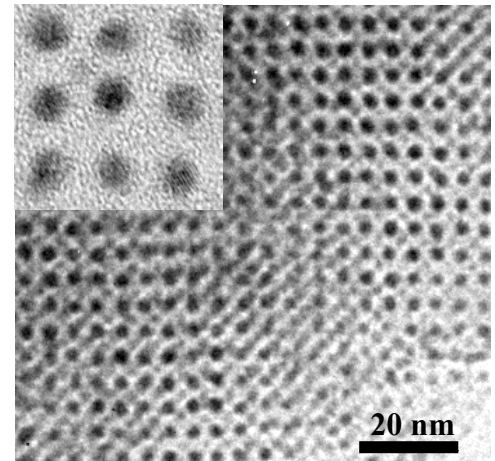
Emergent behavior  
(Lu et al. ***Nature***, 2001)

Nanostructuring of conjugated polymers may allow control of charge and energy transfer

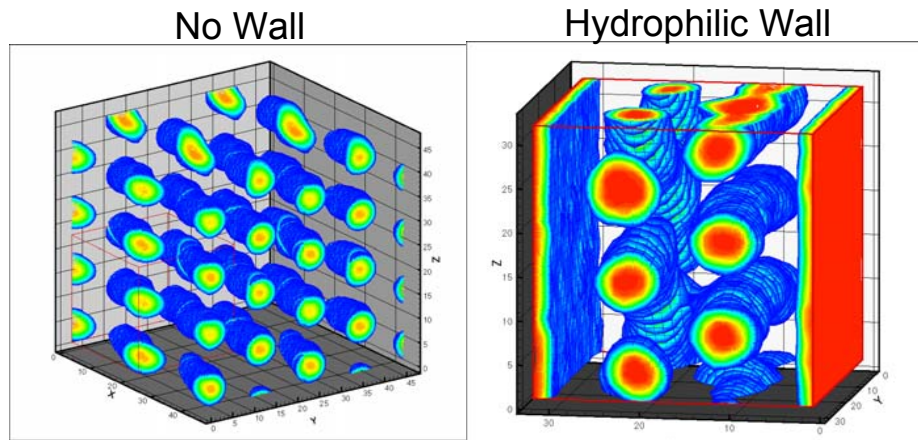
# Nanomaterials Integration: Develop New Function, Understand and Exploit Effects of Interfaces, Dimensional Constraints, Collective Phenomena



**Charge injection into organic single crystal allows single molecule switching**



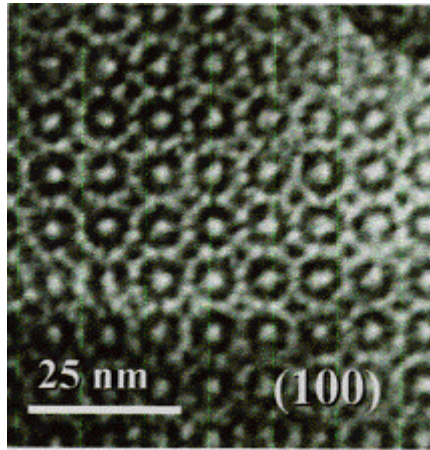
Self-assembly of QDs into robust inorganic nanostructure allows control of 3-D spatial arrangement (other than FCC), conducting to semi-conducting to insulating properties (Fan, Brinker, unpublished)



Orientation achieved through Interfacial interactions (van Swol)

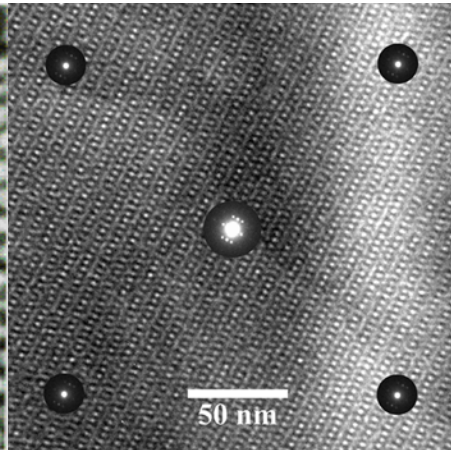
# Evaporation-Induced Self-Assembly Enables Facile, Efficient Nano-Micro-Macro Integration

**Membrane**



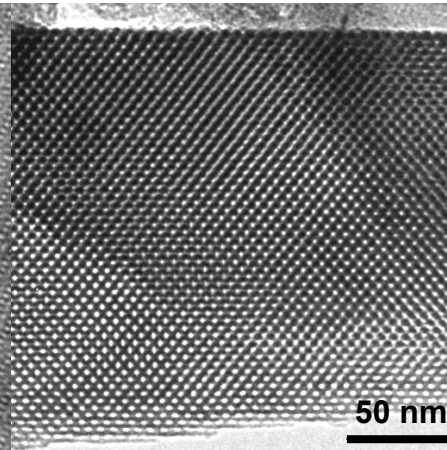
Lu et al., Nature 1997

**Sensor**



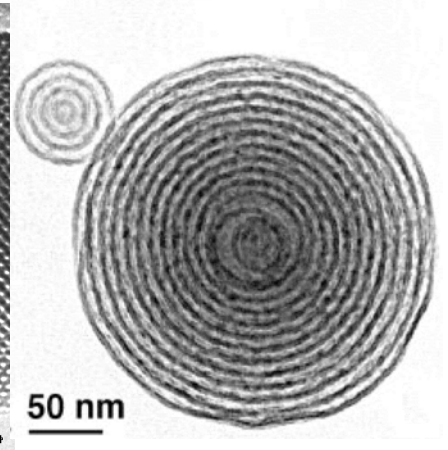
**Ag/Silica  
Nanocomposite**

**low k**



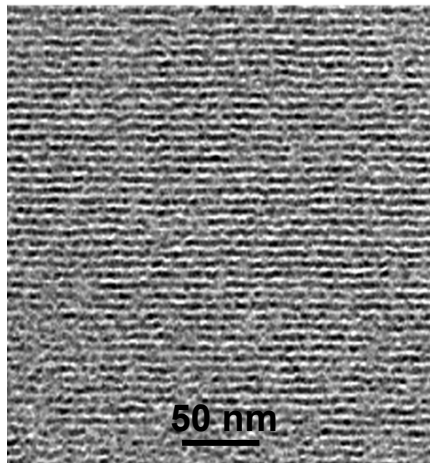
Brinker et al.,  
Adv. Mater. 1999

**Controlled release**

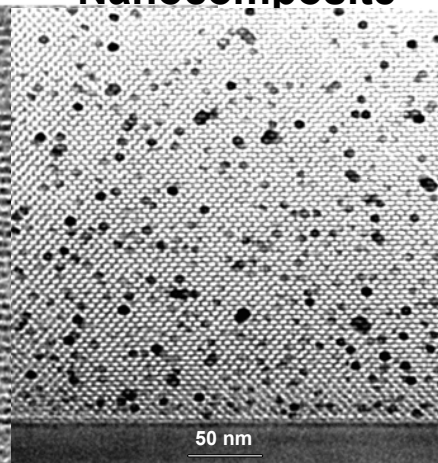


Lu, et al.,  
Nature 1999

**Sea-Shell**

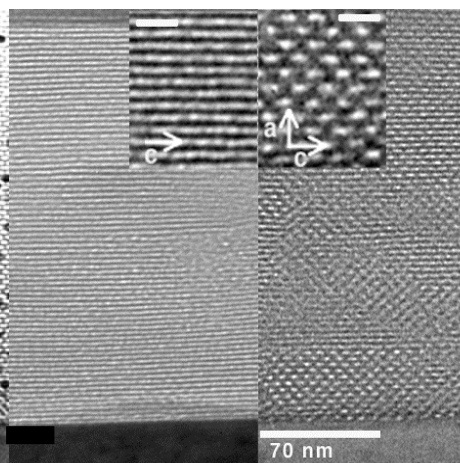


Sellinger et al.,  
Nature 1998



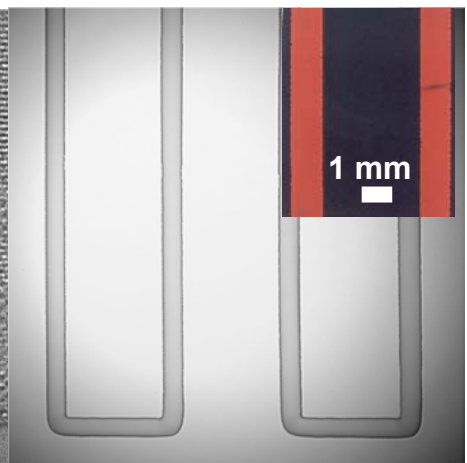
Fan et al.,  
Unpublished

**Phase Transition**



Doshi et al.,  
Science 2000

**Patterns**

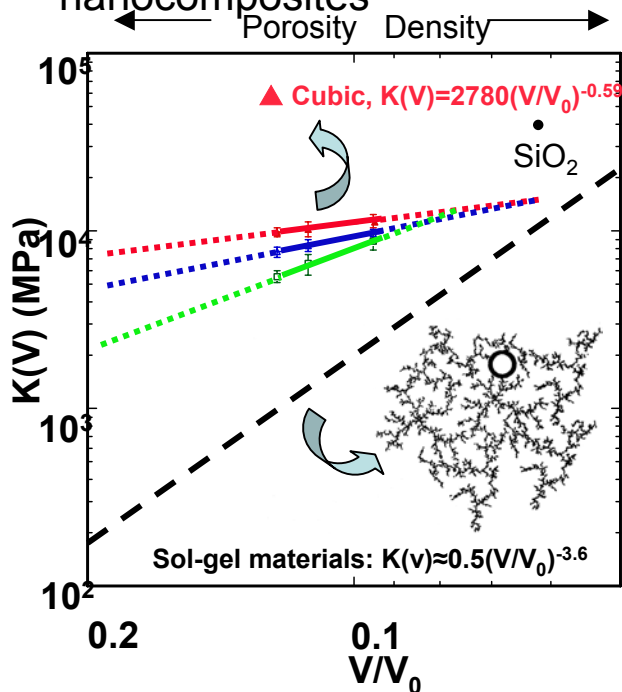


Fan et al.,  
Nature 2000

# The CINT Environment Will Foster Interactions With Other Thrust Areas and the Nanoscience Community

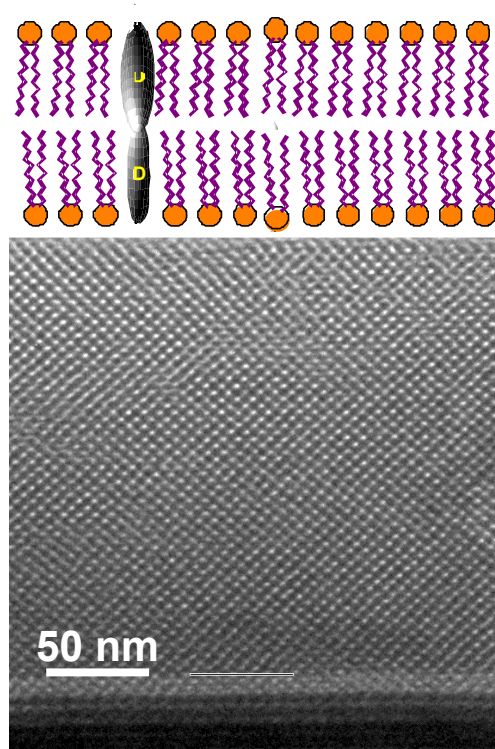
## Nanomechanics (explore limits of continuum Mechanics)

- Investigate/model mechanical behavior of porous and composite nanostructures
- Study mechanochromism in conjugated polymer/inorganic nanocomposites



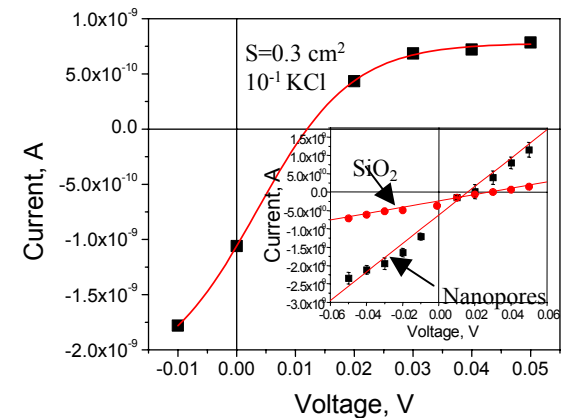
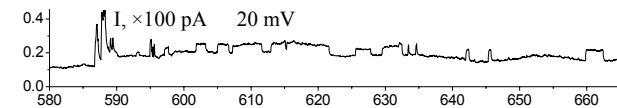
## Nano-bio-micro interfaces (exploit porous architectures as water-filled solid state platforms)

- New porous inorganic platforms for supported lipid bilayers and ion channels



## Nanophotonics (exploit collective behavior)

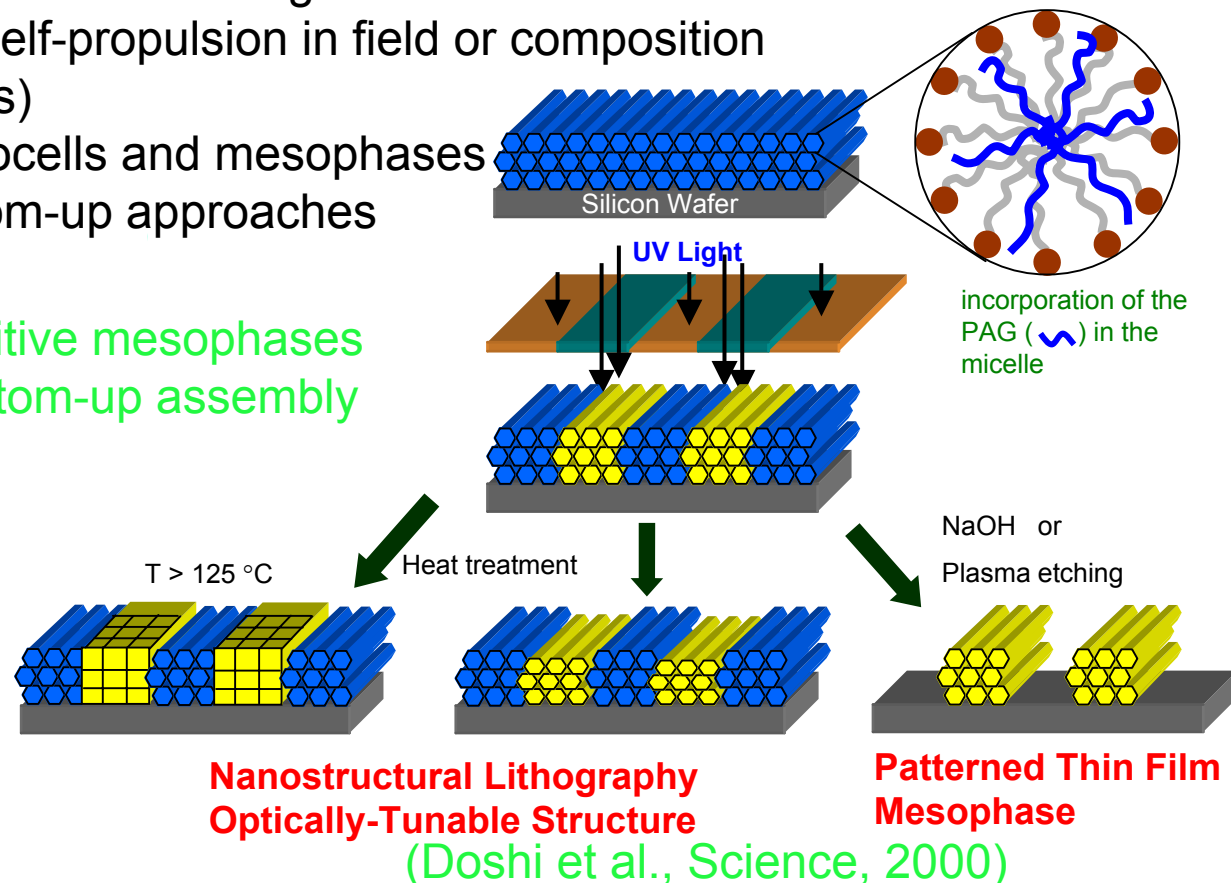
- Large electro-optic responses
- Negative refractive index materials
- Dipolar nanocomposites
- Position QD arrays in photonic band gaps crystals



# CINT Will Promote Discovery of New Materials and Functions

- Extend directed and self-assembly approaches by incorporation of nanocell complexes, quantum dots, and colloids; enhance interfacially-driven phenomena
- Explore complex material designs and/or synthesis procedures that employ or are derived from collective emergent behavior (Brownian ratchets, self-propulsion in field or composition gradients, chemotaxis)
- Serve as a “foundry” for nanocells and mesophases
- Combine top-down and bottom-up approaches

Self-assembly of photosensitive mesophases combines top-down and bottom-up assembly to achieve new functionality



# Complex Functional Nanomaterials - Theory and Simulation

---

## Issues / Challenges

### Materials Design

- Establish structure-property relationships of QDs (material type, size, spacing) and nanocomposites (materials, connectivity, interfacial phenomena) to design new artificial solids
- Understand effects of temperature, pressure, electric fields on synthetic molecular crystals to predict new emergent states and determine origins of microscopic parameters such as carrier density, Fermi velocity, and electron-phonon coupling

### Nanofabrication

- Can we predict self-assembly of multiple materials into complex hierarchical designs?
- What is the influence of extended micro or macro-interfaces, and static or dynamic external fields?

### Materials Performance

- Can we simulate optical, electronic, and transport behaviors of complex functional nanomaterials?

QuickTime™ and a  
decompressor  
are needed to see this picture.

# Complex Functional Nanomaterials - Theory and Simulation

---

## Issues / Challenges

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### Materials Performance

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# Interfaces with the Complex Functional Nanomaterials Thrust

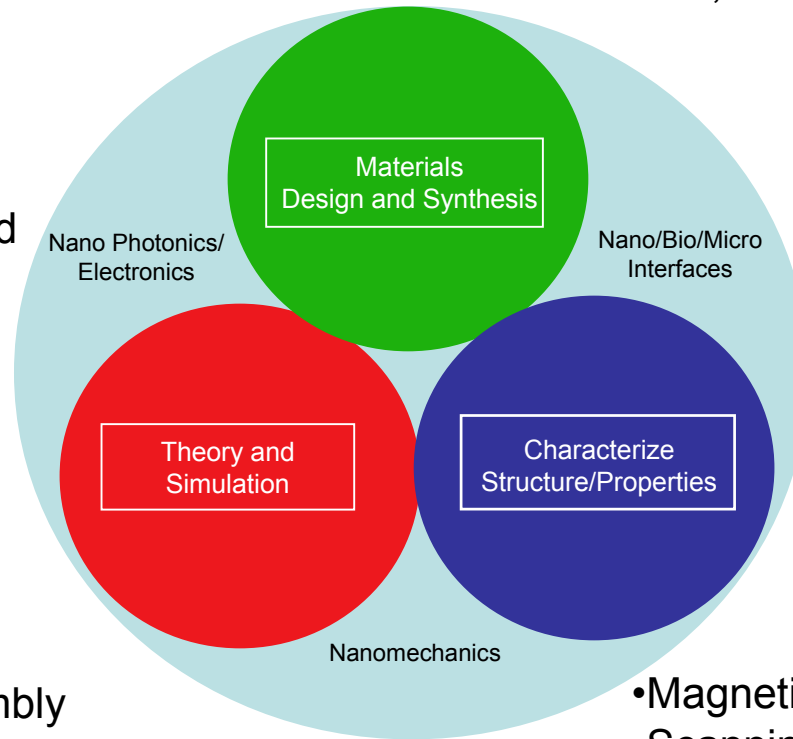
## SNL

- Self-assembled porous and composite nanostructures
  - films
  - particles
- QDs and arrays
- Magnetic field structured solids
- Micromachining / Advanced Lithography
- MBE

- Simulations of self-assembly
    - surfactants
    - colloidal crystallization
    - directed assembly
    - transport behavior
  - Complexity / Collective behavior
- SNL, LANL, S.F. Institute

## LANL

- Crystal growth facility
  - complex nanocell oxides and organics
- QDs, QD molecules, QD solids

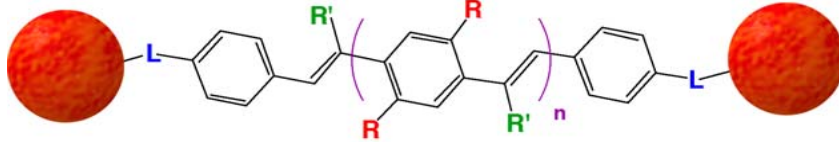


- Magnetic resonance force microscope
- Scanning probe and near field optical microscopies
- Atom tracker
- SANS
- SAXS
- Reflectometry

# Interfaces with the Complex Functional Nanomaterials Thrust

Conjugated backbone can be tuned electronically by addition of a variety of functionalities

Aromatic spacers can be modified to change solubility and the interactions between linkers

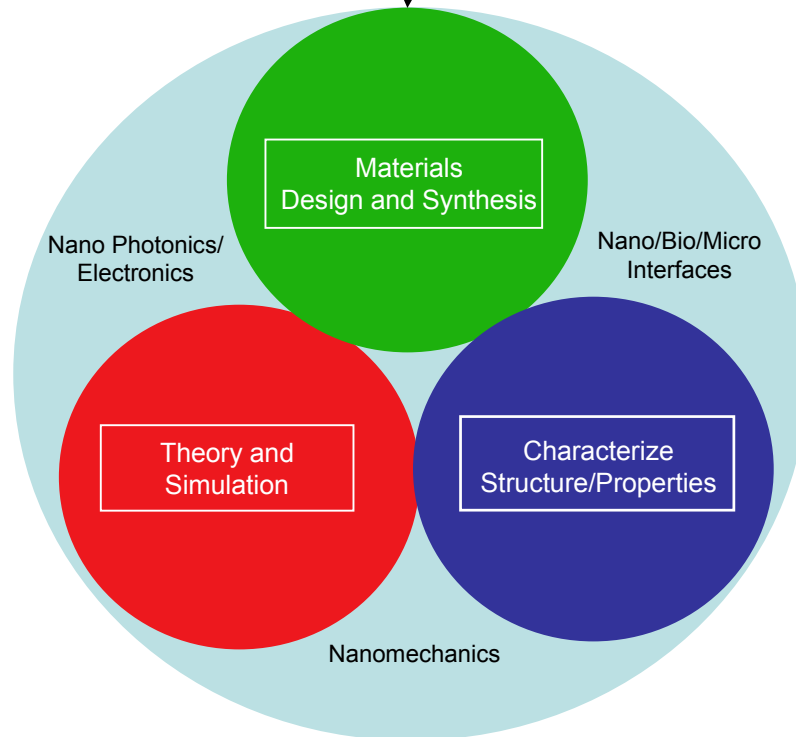


Group has chemical affinity for QD: can be readily modified for QD's of different compositions

The length of the linker can be changed systematically. This provides another method of electronic tuneability

## LANL

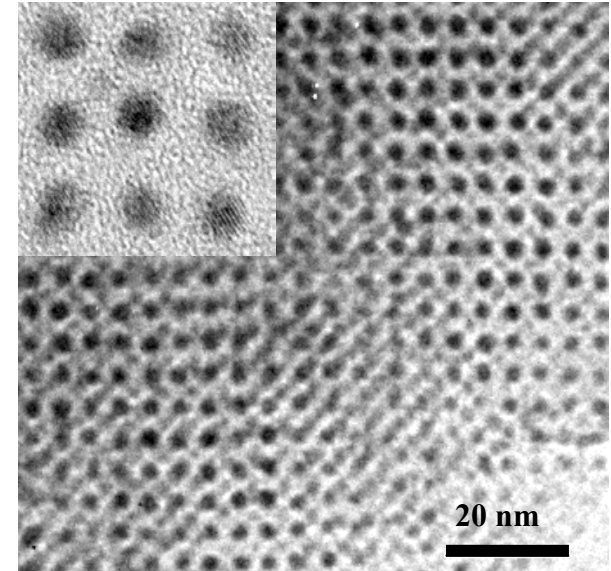
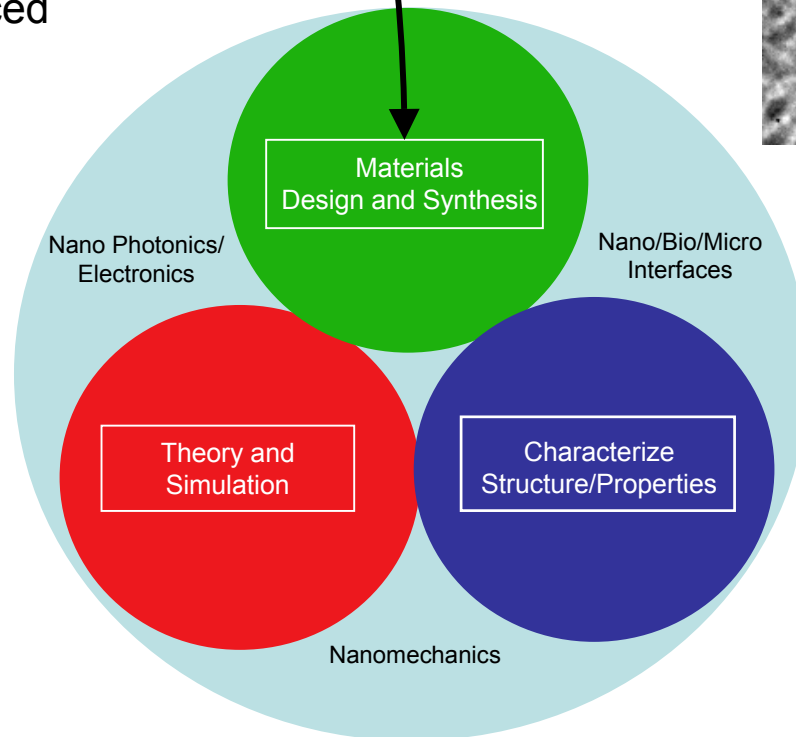
- Crystal growth facility
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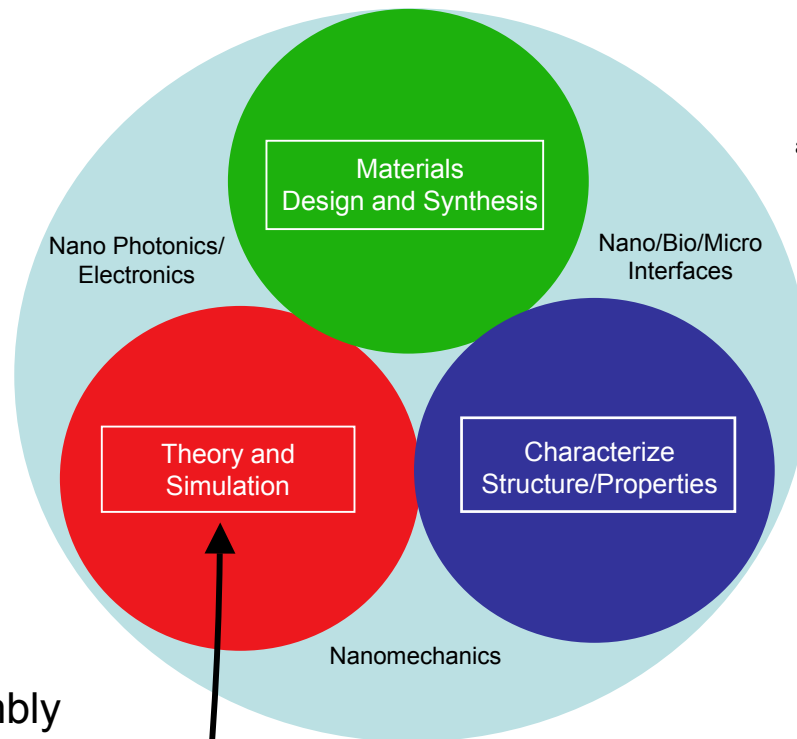
# Interfaces with the Complex Functional Nanomaterials Thrust

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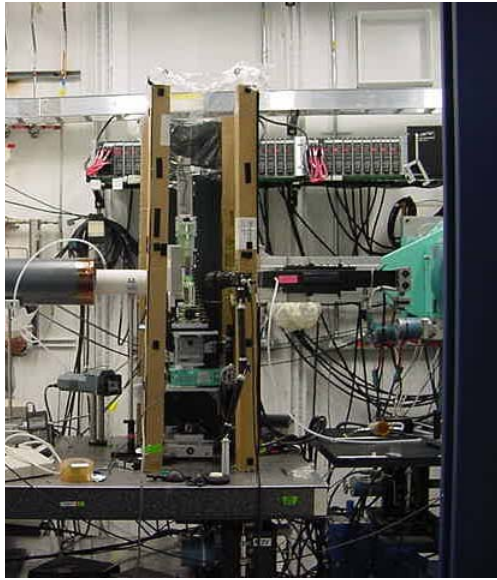
# Interfaces with the Complex Functional Nanomaterials Thrust



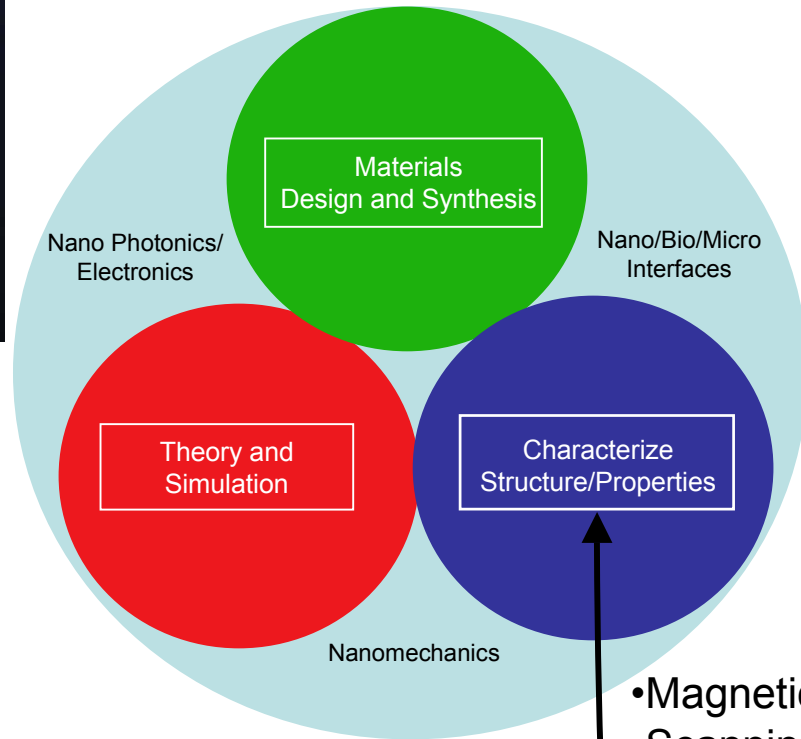
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Video decompressor  
are needed to see this picture.

- Simulations of self-assembly
  - surfactants
  - colloidal crystallization
  - directed assembly
  - transport behavior
- Complexity / Collective behavior  
SNL, LANL, S.F. Institute

# Interfaces with the Complex Functional Nanomaterials Thrust



In situ grazing incidence SAXS of mesophase self-assembly at Argonne's Advanced Photon Source



- Magnetic resonance force microscope
- Scanning probe and near field optical microscopies
- Atom tracker
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- SAXS
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# Interfaces with the Complex Functional Nanomaterials Thrust

## SNL

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